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Modeling a Bioremediation Process of a Petroleum Contaminated Soil Enhanced With NPK Fertilizer and Animal/Plant Derived Organic Manure

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Abstract— *In this study, the potential effects of animal derived organic manure (cow dung, poultry droppings), saw dust and NPK fertilizer on the bioremediation of petroleum hydrocarbon contaminated soil was investigated. The rate of biodegradation was studied for the period of 10 weeks under laboratory conditions. The biodegradation data were fitted to eight models, four of which are based on microbial growth rate and the other four based on order of reaction. Results obtained show that bioremediation with NPK fertilizer and poultry manure followed the logistic growth curve with a constant yield. While treatment with blend of poultry droppings+cow dung+saw dust, occurred with the logistic growth curve with varying yield. It was observed that at optimum addition of NPK fertilizer and poultry manure, the process obeyed same trend as observed when a combination of poultry droppings+cow dung+saw dust was applied. It also revealed bioremediation as basically a first order process at low and moderate addition of biostimulants. NPK fertilizer and poultry manure obeyed first order rate model with ultimate contaminant greater than zero. Again, it was observed that application of NPK fertilizer and animal manure at an increased quantity without combinations offer similar effect with poultry droppings+cow dung+saw dust. Consequently, the result of the percentage degradation of hydrocarbon for the soil sample studied revealed that the rate of hydrocarbon biodegradation was in the following order (83.5%) > (72.6%) > (68.31%) for biotreatment with blend of poultry droppings+cow dung+saw dust, poultry manure and NPK fertilizer respectively. The observations from the mathematical models, graphical and numerical fit results show that the proposed models employed in this work rather than the usual first order rate model were effective in predicting the bioremediation process.*

Keywords— *Modeling, bioremediation, organic manure, NPK fertilizer, reaction rate order*.

I. INTRODUCTION

The pollution of soil and subsurface environment by petroleum product is a major concern in the industrial world (Agarry, 2010). This is as a result of frequent industrial activities, rapid industrialization and increasing demand for petroleum hydrocarbons and hydrocarbon derived products. Petroleum spills arise from vandalism, sabotage of oil facility sites and installations, corrosion of aged oil facilities via uncontrolled spillage in oil refineries, and storage tanks that pose inevitable damage to our immediate environment. It is very important to realize that, the discharge of hydrocarbons into the environment by transportation via tankers and barges does not limit crude oil spillage only to oil producing areas, but also to neighboring locations that are prone to the risk of oil spill due to transportation accidents and ruptured pipeline network that runs across such areas. Oil spill pollution could also result from the sales and uses of petroleum products, pipeline overflow, breakage and storage tank spill (Obire, 1996). The contamination of soil by crude oil and petroleum products has become a serious problem that represents a global concern for the potential consequences on ecosystem and human health (Onwurah et al., 2007). This oil spills alters the physicochemical properties of the soil, making it impossible for the soil to produce at its optimal capacity as a result of hardening of the soil structure by the hydrocarbons.

Depending on the degree of contamination and remediation measures taken, such environment may remain unsuitable for crop growth for a very long time. The sustainability of soil is of an immense interest and concern to man because of the direct reliance of man's existence on soil. This, therefore serve as an essential reason why soil quality, fertility and productivity should be continually maintained and monitored.

Finding solutions to oil polluted soils has always been the subject of several studies (Leahy et al., 1999). A wide range of remediation measures have been proffered with the aim of offering solution to the damages caused by crude oil on nature of the soil and its physiochemical characteristics. Over the decades, the biological methods of cleaning up the environment have received much attention. This is because of its potential to reduce, detoxify and mineralize chemical pollution, restoring chemical balance at low cost.

Bioremediation is defined as the use of living micro-organisms to breakdown or degrade petroleum hydrocarbon into harmless products such as CO_2 and H_2O. Bioremediation is characterized by lots advantages such as its cost effectiveness, environmental friendliness, simplicity in technology, conservation of soil texture and properties and its ability to produce harmless end products. This is contrary to other physical and chemical treatment methods whose limitations include; transfer of pollutants from one place/phase to another, being a complex technology and expensive to implement at full scale (Vidalis, 2001). Due to the limitations of the physiochemical technologies stated above, great deal of literature has reported that bioremediation methods are alternative and/or supplements to these methods. The bio stimulants involved in this study include; cow dung, poultry droppings, saw dust and inorganic fertilizers (NPK).

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Nigeria is blessed with domestic birds and livestock such as fowl, ram, sheep, cow, goat, etc. These livestock produce waste "dungs", and are abundant in the cattle markets (i.e slaughter houses) and are considered waste. These wastes are considered useless to the ordinary man, but research has shown that such wastes are useful material to modify the soil physical and chemical properties and to release nutrients for a longer period of time. These animal wastes are thus used as bio stimulants to provide and maintain favorable conditions for the growth of the soil microorganisms (Allard et al, 1997). Bio stimulation has been proven to be a promising bioremediation technique for the treatment of polluted soil (Rosenberg et al., 1992).

Mathematical modeling is an important tool in analyzing and understanding environmental systems and process performance. Wherever many process of physical, chemical or biological nature interact with each other, mathematical models provide a rational frame work to formulate and integrate the knowledge that has been otherwise derived from (i) theoretical work (ii) fundamental (e.g laboratory investigations) and site specific experimental works. Nevertheless, when bioremediation strategies are applied, modeling often regard contaminant degradation (concentration), substrate consumption, and microbial growth rate/counts e.t.c.

In this study, bioremediation experiment on a petroleum contaminated soil was carried out; investigating the effect of inorganic fertilizer (NPK), poultry droppings and the mixture of poultry droppings, cow dung, and saw dust ash towards enhancing microbial biodegradation of hydrocarbon polluted soil. This work seeks to utilize relevant models representing the bioremediation of a petroleum contaminated soil under selected treatments including (poultry droppings, cow dung, saw dust and NPK fertilizer). These were ascertained, using the kinetic rate model and substrate dependent model.

II. Research Methodology

2.1 Experimentation

2.1.1 Description of study region

The soil samples used for this study were collected from an oil polluted site of Agbada flow station, located at Mkpokwu manifold, Kpokwudi Community of Rivers State, Nigeria. The oil spill was reported to have occurred in January 2012 while the soil samples were collected from the same site in May 2012 when clean-up exercise has not commenced.

2.1.2 Materials used for the bioremediation study

The following materials were utilized in the course of this study, they include:

- Petroleum contaminated soil
- Inorganic fertilizer (NPK)
- Cow dung (CD)
- Poultry dropping (PD)
- Saw dust (SD)

2.1.3 Soil sample/manure collection

Soil samples used for this study were collected with a shovel at a depth of (0-15cm) from the oil spilled site. The uncontaminated soil sample was collected from an unpolluted site close to the spilled site. The poultry manure was collected from a local poultry farm situated at Umuchichi of Osisioma Ngwa North L.G.A. in Abia State, while the cow dung were obtained from a slaughter market located at Ogbor Hill in Obi Ngwa L.G.A. of Abia State. The NPK fertilizer was purchased from a standard Agrochemical shop at Eke-Akpara Market, Aba, while the saw dust was obtained from a timber market.

2.1.4 Soil sample/manure preparation

The soil samples were sun-dried for three weeks after which it was ground into powder and sieved with 2mm mesh sieve. The sieved soil samples were then used for laboratory analysis. The cow dung and the poultry droppings were also sun dried for three week after which they were ground into powder, sieved through 2mm standard mesh, and some samples were sent to the laboratory for the determination of the mineral content such as carbon, nitrogen and phosphorus. This was carried out to ascertain the remediating properties of the organic manure used. The saw dust was also sun dried for three weeks, passed through 2mm standard mesh, and thereafter some were taken for analysis of the mineral constituents, as presented in table 3.1.

2.1.5 Experimental procedure

The bioremediation study took place from the month of May to July, 2012. The contaminated soil samples used were treated as shown in table 2.1 below. The treatment was subdivided into three options. Each of the treatment options 1-3 constitutes five (5) polyethylene bags each to which were applied different levels of manure/fertilizer. The objective of the variation in the treatment levels was to investigate the most appropriate quantity of each treatment option that will give the best result and then compare their effectiveness.

Option 1 had different levels of NPK fertilizer application, option 2 received different quantities of poultry manure, option 3 had application of varied quantity of a blend of poultry droppings + cow dung and saw dust mixed in equal ratio.

The set-ups of treatments are as follows:

Option 1: The five constituent polyethylene bags in this option received 10g, 20g, 30g, 40g and 50g of 20:10:10 NPK fertilizer which was applied five (5) times at two weeks interval during the ten week study period.

Option 2: The option 2 involves five constituent polyethylene bags with the application of poultry manure. Each of the five constituent polythene bags in this option received 10g, 20g, 30g, 40g and 50g of a poultry manure which were applied five times during the ten-week remediation study and at two weeks interval.

Option 3: The five constituent polyethylene bags in this option had the application of a blend of (poultry + cow) manure and saw dust mixed in equal ratio. 10g, 20g, 30g, 40g and 50g of the mixed manure was applied to each polythene bag at two weeks interval for the period of ten weeks.

Table 2.1. Experimental design for the bioremediation study

Options	**Treatment/biostimulants**
Option 1	Contaminated soil + NPK fertilizer (F_A)
Option 2	Contaminated soil + poultry manure (F_B)
Option 3	Contaminated soil + (poultry + cow) manure + saw dust (F_c)

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The experimental layout is shown in Table 2.2 below;

Table 2.2. Experimental layout

Option 1	F_{A1}	F_{A2}	F_{A3}	F_{A4}	F_{A5}
Option 2	F_{B1}	F_{B2}	F_{B3}	F_{B4}	F_{B5}
Option 3	F_{C1}	F_{C2}	F_{C3}	F_{C4}	F_{C5}

Where:

F_A - NPK (20:10:10) fertilizer
F_B - Poultry manure
F_C - (Poultry + cow+ saw dust) manure
F_{A1} - Polythene bag with 10g of NPK (20:10:10) fertilizer
FA2 - Polythene bag with 20g of NPK (20:10:10) fertilizer
F_{A3} - Polythene bag with 30g of NPK (20:10:10) fertilizer
F_{A4} - Polythene bag with 40g of NPK (20:10:10) fertilizer
F_{A5} - Polythene bag with 50g of NPK (20:10:10) fertilizer
F_{B1} - Polythene bag with 10g of poultry manure
F_{B2} - Polythene bag with 20g of poultry manure
F_{B3} - Polythene bag with 30g of poultry manure
F_{B4} - Polythene bag with 40g of poultry manure
F_{B5} - Polythene bag with 50g of poultry manure
FC_1 - Polythene bag with 10g of (poultry + cow) manure + saw dust
F_{C2} - Polythene bag with 20g of (poultry + cow) manure + saw dust
F_{C3} - Polythene bag with 30g of (poultry + cow) manure + saw dust
F_{C4} - Polythene bag with 40g of (poultry + cow) manure + saw dust
F_{C5} - Polythene bag with 50g of (poultry + cow) manure + saw dust

This research work was conducted for 10 weeks, during which samples were taken to the laboratory for analysis once in every two weeks.

2.1.6 Soil characterization/physicochemical analysis

The soil samples and the various biostimulants were characterized for some physical and chemical properties such as soil pH, Total Organic Carbon (TOC), Total Organic Matter (TOM), Total Nitrogen (N), Total Phosphorous (P), Total Potassium (K), Moisture Content, Total Petroleum Hydrocarbon (TPH), according to the standard methods adopted by the Research and Development Center (RDC) of Nigeria National Petroleum Company (NNPC).

2.2. Model Formulation Based on Microbial Growth

Oyoh and Osoka (2007), based on certain assumptions developed some models which they fitted to experimental data from NPK fertilizer enhanced bioremediation. The models include:

- If microbial growth is exponential and yield is constant (Model 1):

$$S = S_o + \frac{x_0}{Y_G}(1 - e^{\mu t}) \qquad 2.1$$

- If microbial growth is exponential and yield is not constant (Model 2):

$$S_o = S_o (e^{\mu t})^{\frac{1}{Y_G}} \qquad 2.2$$

- If microbial growth is Logistic growth with constant yield (Model 3)

$$S = S_O + \frac{x_0}{Y_G}\left(1 - \frac{e^{\mu t}}{1-\gamma x_0\left(1-e^{\mu t}\right)}\right) \qquad 2.3$$

- If microbial growth is Logistic growth with yield not constant (Model 4):

$$S_o = S_o \left(\frac{e^{\mu t}}{1-\gamma x_0\left(1-e^{\mu t}\right)}\right)^{\frac{1}{Y_G}} \qquad 2.4$$

Where, S = substrate concentration TPH, (mg/kg)
So = Initial substrate concentration (initial TPH)
x_0 = Initial microbial concentration
Y_G = Yield coefficient
μ = Specific growth rate of the microbes
γ = Inverse of the maximum microbial concentration.
t = Time (weeks)

These models were preferentially selected and used in fitting the experimental data from this research, as a way of verifying their suitability for bioremediation studies.

2.3. Model Formulation Based on Reaction Order

First order kinetics is commonly used to describe biodegradation in environment fate model because mathematically the expression can be incorporated easily into models (Greene et al, 2000). In the same trend, many researchers grasp at first order kinetics because of the ease in presenting and analyzing the data, the simplicity in plotting the logarithm of the rate of chemical reaction versus time as a straight line and the ease in predicting future concentrations.

In a different focus, first order rate model may not be suitable. In this case different models can be formulated to suit bioremediation process and this can be achieved based on several reasonable assumptions.

In this study, the bioremediation can be generally represented as an nth reaction rate order.

Thus;

$$\frac{ds}{dt} = -k(s - s_\infty)^n \qquad 2.5$$

where, S = substrate (contaminant) concentration at any time
$S\infty$ = the ultimate substrate (contaminant) Concentration
K = the reaction rate constant (week^{-1}).
t = time (weeks)
n = the order of the reaction (Osoka and Onyelucheya, 2010)

Model 1:

If the reaction order is zero order, equation 2.5 becomes;

$$\frac{ds}{dt} = -k\left(s - s_\infty\right)^0 \qquad 2.6$$

integrating within the limits of $s(t=o) = s_{o,}$ and $s(t) = s$, we have

$$\int_{s_0}^{s} ds = -k\int_{o}^{t} dt \quad 2.7$$

$$s - s_0 = -kt$$

therefore;

$$s = s_0 - kt \quad 2.8$$

Where s_0 is the initial substrate (contaminant) concentration.

Model 2:

If the reaction is first order, equation 2.9 becomes;

$$\frac{ds}{dt} = -k\left(s - s_\infty\right) \quad 2.9$$

Integrating under similar limits as in model 1 above,

$$\frac{ds}{dt} = -k\int_{o}^{t} dt$$

$$\ln(s - s_\infty)^s = -kt$$

$$\ln\left(\frac{s - s_\infty}{s_0 - s}\right) = -kt \quad 2.10$$

Assuming bioremediation eventually remove all (contaminant) such that the ultimate (contaminant) concentration becomes zero, that is $s_{\infty=0}$, equation 2.10 becomes;

$$\frac{ds}{dt} = e^{-kt}$$

$$s = s_0\, e^{-kt} \quad 2.11$$

Model 3:

If the ultimate contaminant concentration is not zero, i.e $(s_{\infty\neq 0})$

$$s - s_\infty = \left(s_0 - s\right)e^{-kt}$$

$$s = s_\infty + \left(s_0 - s_\infty\right)e^{-kt} \quad 2.12$$

Model 4:

If the reaction is second order, equation 2.5 becomes;

$$\frac{ds}{(s - s_\infty)^2} = -k\, dt \quad 2.13$$

Integrating within the same limits as in model 1, equation 2.13 becomes:

$$\frac{s_0 - s}{s - s_\infty} = \left(s - s_\infty\right)kt \quad 2.14$$

If the ultimate contaminant concentration is zero (s_∞ = 0), then;

$$\frac{s_0 - s}{s} = s_0 kt$$

$$\frac{s_0}{s} = 1 + s_0 kt$$

$$s = \frac{s_0}{1 + s_o kt} \quad 2.15$$

III. Results and Discussion

3.1. Results Presentation

Table 3.1. Results of nutrient analysis and soil physicochemical properties before remediation

	BEFORE REMEDIATION					AFTER REMEDIATION
Parameters	**NPK Fertilize F_A**	**Poultry Manure F_B**	**Poultry+ cow+sawdust F_C**	**Uncontaminated soil**	**Contaminated Soil sample**	**Contaminated Soil sample**
pH	6.5	7.13	7.25	6.33	4.70	8.36
Nitrogen	0.5	0.33	0.42	0.13	0.19	0.28
Phosphorous	1.01	0.32	0.36	6.10	3.42	5.14
Organic Carbon (%)	21.3	22.2	26.2	1.34	4.03	5.35
Organicmatter (%)	4.30	6.21	9.18	3.08	4.33	5.83
Organic C/N Ratio				14.6:1	25.81	34.66
THC (mg/kg)	/	/		3.14	1980	
% sand	/	/		83.31	83.10	
% Silt	/	/		1.22	1.44	
% clay	/	/		15.47	15.49	

3.1.1 Graphical fit results for models based on microbial growth

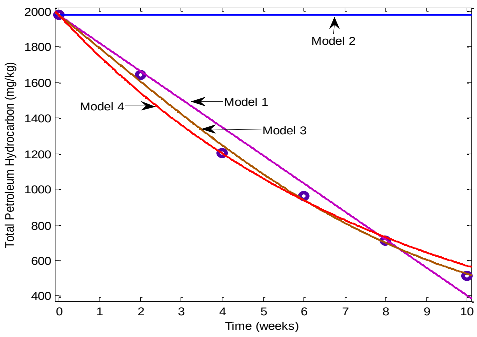

Fig. 3.1. Total petroleum hydrocarbon versus time for 10g of npk fertilizer

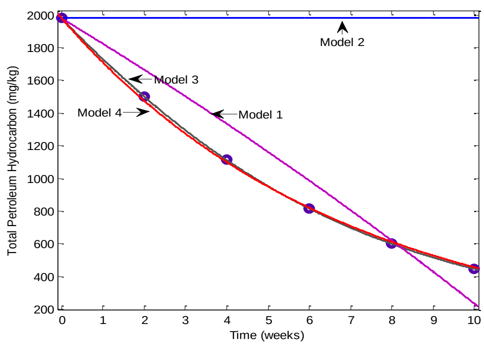

Fig. 3.2. Total petroleum hydrocarbon versus time for 20g of npk fertilizer

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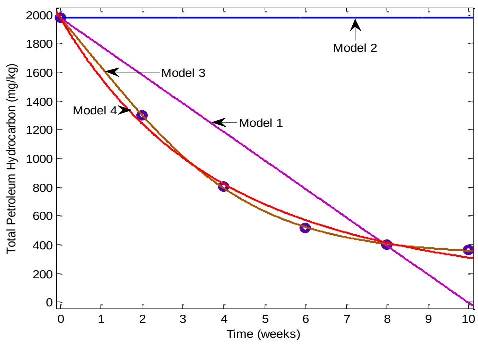

Fig. 3.3. Total petroleum hydrocarbon versus time for 30g of npk fertilizer

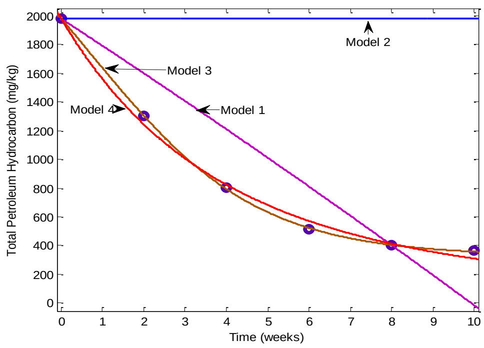

Fig. 3.4. Total petroleum hydrocarbon versus time for 40g of npk fertilizer

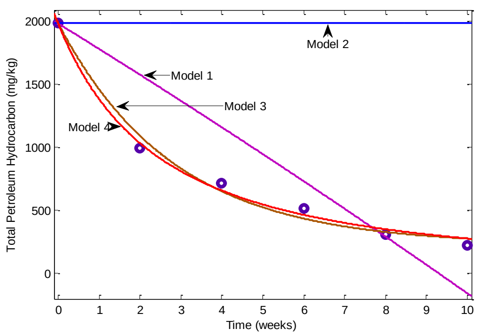

Fig. 3.5. Total petroleum hydrocarbon versus time for 50g of npk fertilizer

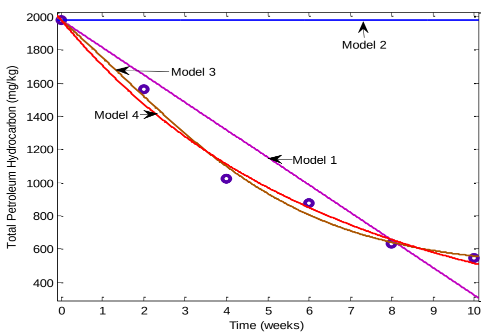

Fig. 3.6. Total petroleum hydrocarbon versus time for 10g of poultry manure

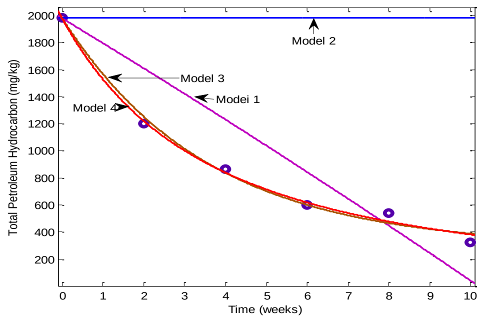

Fig. 3.7. Total petroleum hydrocarbon versus time for 20g of poultry manure

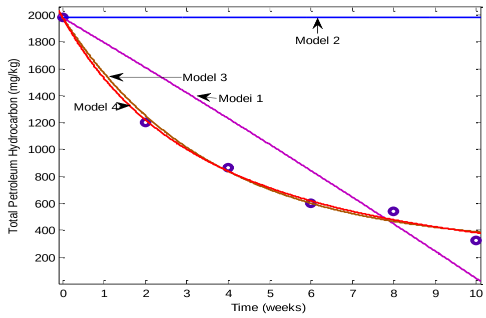

Fig. 3.8. Total petroleum hydrocarbon versus time for 30g of poultry manure

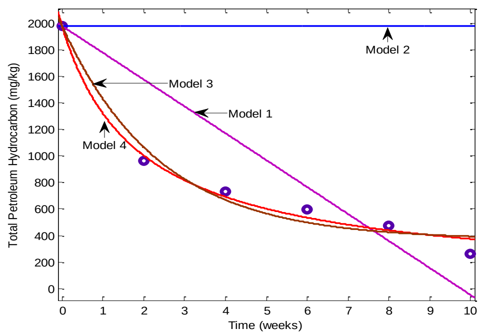

Fig. 3.9. Total petroleum hydrocarbon versus time for 40g of poultry manure

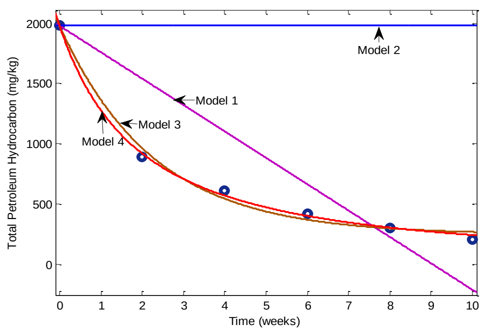

Fig. 3.10. Total petroleum hydrocarbon versus time for 50g of poultry manure

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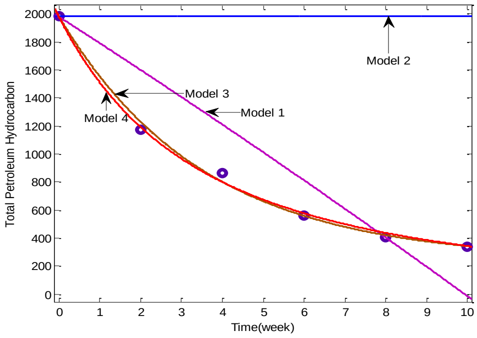

Fig. 3.11. Total petroleum hydrocarbon versus time for 10g of (poultry+cow+sawdust) manure

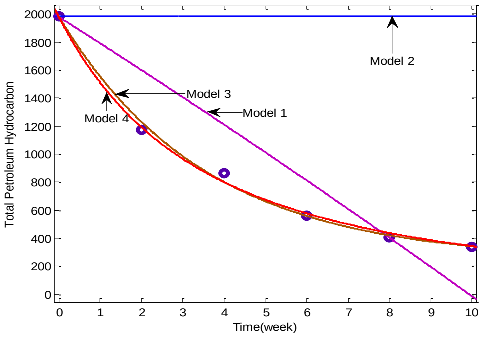

Fig. 3.12. Total petroleum hydrocarbon versus time for 20g of (poultry+cow+sawdust) manure

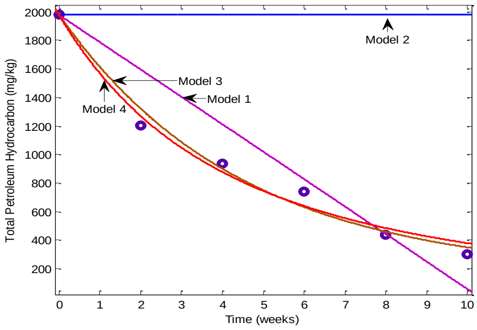

Fig. 3.13. Total petroleum hydrocarbon versus time for 30g of (poultry+cow+sawdust) manure

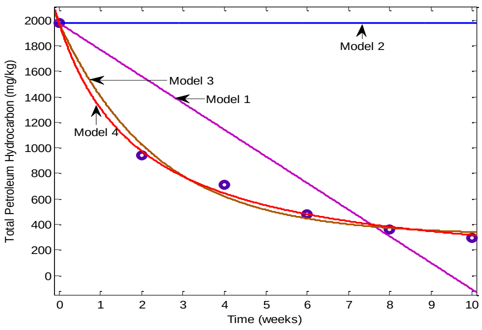

Fig. 3.14. Total petroleum hydrocarbon versus time for 40g of (poultry+cow+sawdust) manure

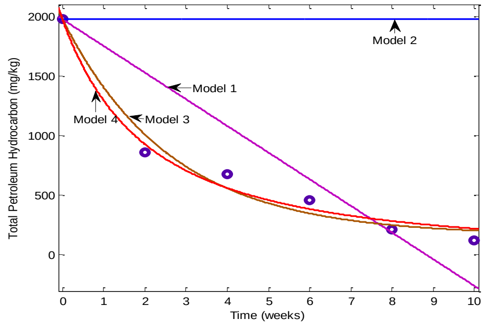

Fig. 3.15. Total petroleum hydrocarbon versus time for 50g of (poultry+cow+sawdust) manure

3.1.2 Graphical fit results for models based on order of reaction

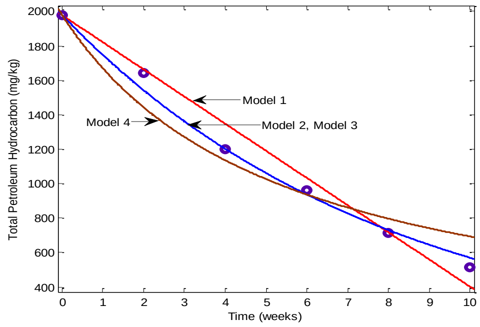

Fig. 3.16. Total petroleum hydrocarbon versus time for 10g of npk fertilizer

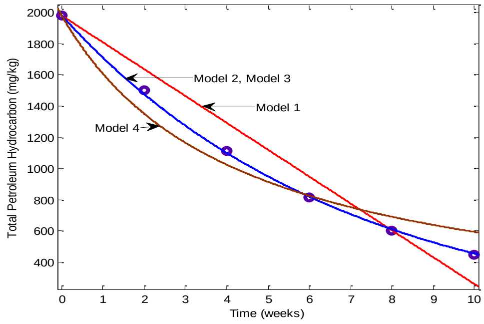

Fig. 3.17. Total petroleum hydrocarbon versus time for 20g of npk fertilizer

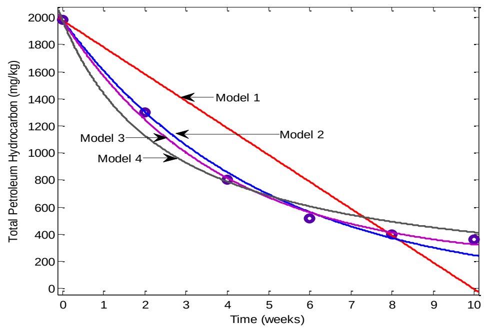

Fig. 3.18. Total petroleum hydrocarbon versus time for 30g of npk fertilizer

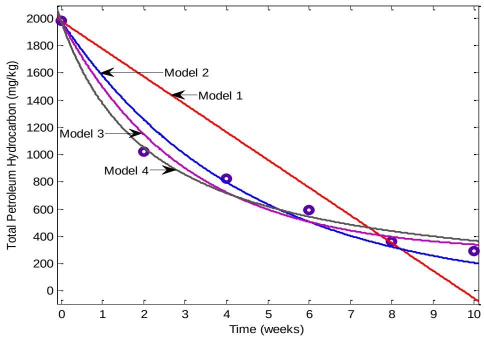

Fig. 3.19. Total petroleum hydrocarbon versus time for 40g of npk fertilizer

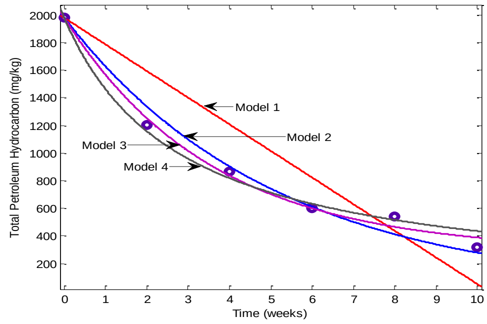

Fig. 3.23. Total petroleum hydrocarbon versus time for 30g of poultry manure

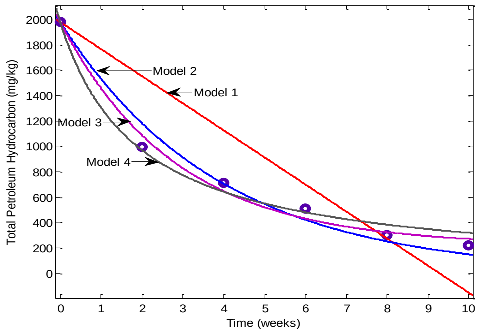

Fig. 3.20. Total petroleum hydrocarbon versus time for 50g of npk fertilizer

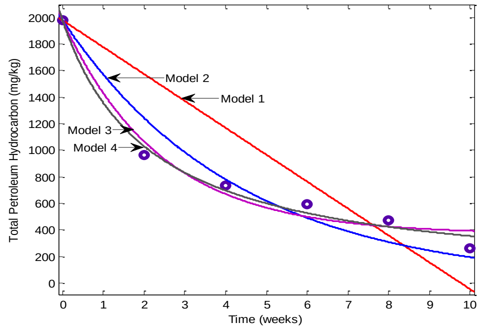

Fig. 3.24. Total petroleum hydrocarbon versus time for 40g of poultry manure

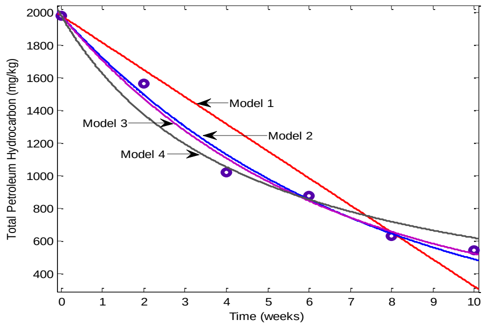

Fig. 3.21. Total petroleum hydrocarbon versus time for 10g of poultry manure

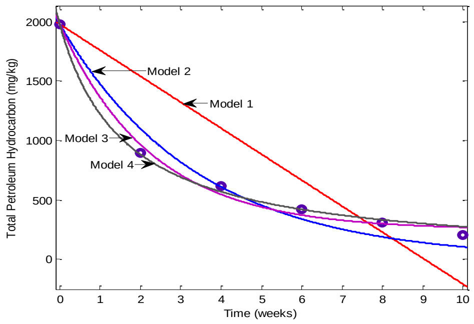

Fig. 3.25. Total petroleum hydrocarbon versus time for 50g of poultry manure

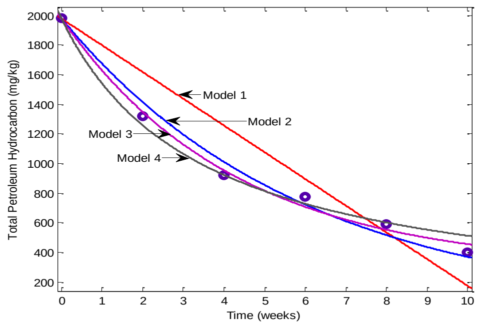

Fig. 3.22. Total petroleum hydrocarbon versus time for 20g of poultry manure

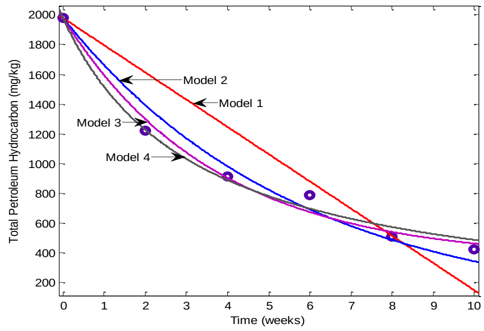

Fig. 3.26. Total petroleum hydrocarbon versus time for 10g of (poultry+cow+sawdust) manure

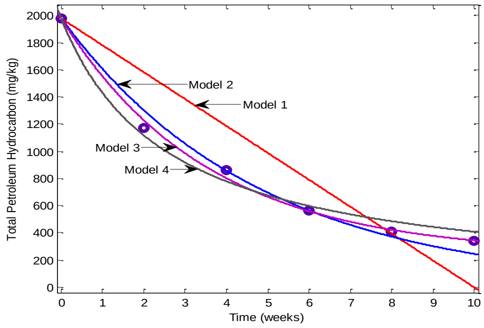

Fig. 3.27. Total petroleum hydrocarbon versus time for 20g of (poultry+cow+sawdust) manure

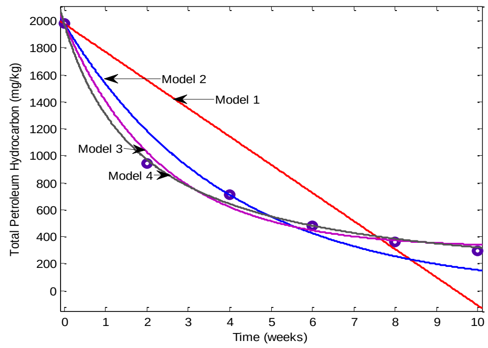

Fig. 3.29. Total petroleum hydrocarbon versus time for 40g of (poultry+cow+sawdust) manure

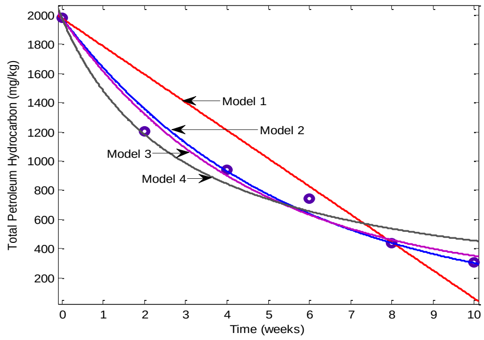

Fig. 3.28. Total petroleum hydrocarbon versus time for 30g of (poultry+cow+sawdust) manure

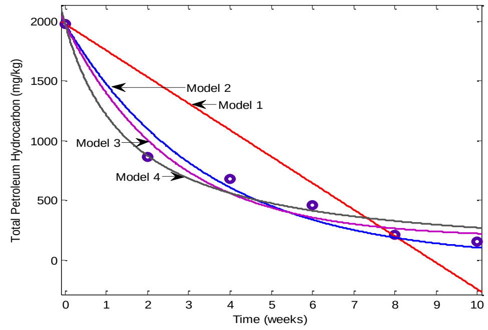

Fig. 3.30. Total petroleum hydrocarbon versus time for 50g of (poultry+cow+sawdust) manure

3.1.3 Numerical fit results for the models based on microbial growth

Table 3.2. Parameter values and numerical fit results for treatment with NPK fertilizer, (F_A)

Quantity of fertilizer(g)	S_o (mg/kg)	Y_G	X_o/Y_G	μ	γX_0	R^2	RMSE	SSE
10-E_1	1980		0.000000172	0.00000915		0.6532	100.4	0.000028
E_2		71.87		0.0000222		-2.529	1050	0.00000551
E_3			0.00001320	0.2408	0.4239	0.9764	36.81	4.0644
E_4		0.002009		0.00000034	67.76	0.9913	67.4	1.3638
20-E_1	1980		0.00000191	0.02584		0.9106	194.3	0.0000051
E_2		69.36		0.00000000176		-2.899	1148	0.0000066
E_3			0.000001468	0.02584	0.6614	0.9963	2.428	1.7695
E_4		0.001702		0.2117	46.91	0.9954	19.08	1.0922
30-E_1	1980		0.00000175	0.002044		0.8864	153.6	0.000037
E_2		74.02		0.00000003435		-2.628	1226	0.0000042
E_3			0.0001899	0.491	0.4152	0.9985	6.378	0.106
E_4		0.00164		0.05957	1.001	0.9952	56.79	0.9677
40-E_1	1980		0.00000136	0.002135		0.8895	132.4	0.0000056
E_2		62.05		0.000000422		-2.224	1250	0.0000044
E_3				0.491	0.4152	0.9997	5.344	0.164
E_4		0.001522	0.0001682	0.05957	1.001	0.9920	47.79	0.877
50- E_1	1980	60.13	0.00000132	0.003231		0.9254	108.8	0.00000047
E_2				0.00000063		-2.662	1299	0.00000533
E_3		0.001361	0.0001437	0.356	0.991	1	5.067	0.116
E_4				0.0001261	2.130	0.9962	43.82	0.646

E_1 = Biomass Growth model equation 1, E_2 = Biomass Growth model equation 2, E_3 = Biomass Growth model equation 3, E_4 = Biomass Growth model equation 4

Table 3.3. Parameter values and numerical fit results for treatment with poultry manure, (F_B)

Quantity of poultry manure (g)	S_o (mg/kg)	Y_G	X_o/Y_G	μ	YX_0	R^2	RMSE	SSE
10-E_1	1980		0.0000485	0.0000482		0.7162	25.16	0.0000017
E_2		74.2		0.00000212		-3.316	12.66	0.000000723
E_3			0.00000144	0.4023	0.3586	0.9919	44.97	1.215
E_4		0.4516		0.00005.305	473.6	0.9804	78.5	5.766
20-E_1	1980		0.0000147	0.00109		0.7214	27.47	0.00000262
E_2		72.08		0.0000224		-3.512	12.18	0.00001136
E_3			0.00000164	0.236	0.9899	0.9934	61.54	0.1336
E_4		0.614		0.0001525	747.9	0.9952	51.46	7.994
30-E_1	1980		0.00001568	0.01165		0.6917	23.37	0.0000446
E_2		65.71		0.0000004131		-3.713	11.09	0.000000856
E_3			0.00000172	0.2826	0.9002	0.9924	57.89	1.3834
E_4		0.597		0.0002017	711.2	0.9950	54.96	5.4061
40-E_1	1980		0.0000171	0.00117		0.6204	22.96	0.000000972
E_2		62.82		0.00000000344		-4.243	10.95	0.00007042
E_3			0.00000133	0.4226	0.980	0.9817	32.29	0.000428
E_4		0.507		0.0002357	307.1	0.9969	49.5	2.0082
50-E_1	1980		0.0000000174	0.0001269		0.5833	1.994	0.000000090
E_2		63.01		0.00000000354		-4.306	10.31	0.000000014
E_3			0.000000189	0.4617	0.991	0.9985	28.25	0.0000611
E_4		0.456		0.0003074	191.1	0.9996	37.47	2.004211

Table 3.4. Parameter values and numerical fit results for treatment with (poultry+cow+saw dust) manure, (F_C)

Quantity of (poultry+cow+Sawdust) (g)	S_o (mg/kg)	Y_G	Xo/Y_G	μ	YX_0	R^2	RMSE	SSE
10-E_1	1980		0.0000156	0.00012106		0.5564	310	0.00000384
E_2		62.06		0.00000000499		-4.306	12.42	0.0000000774
E_3			0.0000975	0.211	0.9983	0.9865	85.65	0.0000161
E_4		0.784		0.0000382	1553	0.991	69.44	1.04069
20-E_1	1980		0.0000156	0.001196		0.7433	350.2	0.0000049o4
E_2		73.29		0.00001863		-3.745	13.47	0.0009077
E_3			0.00000171	0.2844	0.9963	0.9963	48.75	0.000007076
E_4		0.784		0.0001588	999.1	0.9972	42.08	5.312
30-E_1	1980		0.00000705	0.000112		0.8375	380.4	0.00000115
E_2		72.22		0.0000222		-3.557	87.73	0.000000027
E_3				0.2246	0.9927	0.9831	101.9	0.00000614
E_4		0.4479	0.00000248	0.00164	667	0.9853	95.02	5.305
40-E_1	1980		0.0000011724	0.000133		0.4965	446.3	0.000007968
E_2		62.89		0.00000000307		-4.274	14.42	0.0000000103
E_3			0.00000337	0.4263	0.9951	0.9901	480.0	0.0000559
E_4		0.6728		0.0001963	2519	0.9965	48.26	3.988
50- E_1	1980		0.0000013	0.0001152		0.5537	407.4	0.00000773
E_2		58.37		0.000000311		-0.412	33.54	0.0000000158
E_3		o.6163	0.000001437	0.484	0.9875	0.9895	138.6	0.00000157
E_4				0.0002509	1.268	1	23.15	3.686

3.1.4 Numerical fit results for the models based on order of reaction

Table 3.5. Model rate constants and numerical fit results for NPK fertilizer, (F_A)

Quantity of fertilizer (g)	R^2	RMSE	K	SSE
10- M_1	-2.3752	15.33	0.0000018	3.31
M_2	0.8574	106	0.0121	2.53
M_3	0.9433	58.19	0.0225	1.35
M_4	0.9669	128.7	0.3335	4.28
20- M_1	-2.6643	18.08	0.0000001175	2.83
M_2	0.8843	118	0.0131	4.12
M_3	0.9771	65.19	0.0235	1.06
M	0.9898	128.7	0.0353	6.08
30- M_1	-2.2442	21.75	0.0001902	4.14
M_2	0.8865	143	0.0146	3.66
M_3	0.9967	44.6	0.0242	6.72
M_4	0.9758	110.3	0.0272	4.88
40-M_1	-0.3422	22.67	0.0002226	1.72
M_2	0.9311	158	0.0151	3.55
M_3	0.9810	95.69	0.2441	3.66
M_4	0.9865	72.17	0.3354	2.63
50- M_1	-0.2843	20.06	0.0002618	3.18
M_2	0.9552	103	0.01553	2.13
M_3	0.9973	75.57	0.0252	2.28
M_4	0.9939	67.19	0.3533	2.25

Where; M_1 = Reaction rate model equation, M_2 = Reaction rate model equation, M_3 = Reaction rate model equation 3, M_4 = Reaction rate model equation

Table 3.6. Model rate constants and numerical fit results for poultry manure, (F_B)

Quantity of poultry manure (g)	R^2	RMSE	K	SSE
10- M_1	-3.2331	14.91	0.0001108	1.26
M_2	0.8884	98.11	0.01165	1.08
M_3	0.9888	66.51	0.02311	0.16
M_4	0.9685	99.53	0.2653	0.00011
20- M_1	-3.4443	23.06	0.000144	3.03
M_2	0.9127	100.29	0.0135	1.21
M_3	0.9932	64.41	0.I338	0.23
M_4	0.9886	78.62	0.2816	0.00014
30- M_1	-3.5452	20.55	0.000179	2.66
M_2	0.9093	118.4	0.0138	2.34
M_3	0.9924	58.56	0.1503	0.28
M_4	0.9897	61.15	0.2031	0.00018
40 M_1	-3.33335	44.14	0.000234	2.32
M_2	0.9514	56.08	0.01388	0.53
M_3	0.9771	103.1	0.1654	0.4183
M_4	0.9887	64.79	0.3335	0.00023
50- M_1	-4.1614	39.83	0.000044	1.17
M_2	0.8896	45.55	0.0156	0.88
M_3	0.9968	67.36	0.1562	0.16
M_4	0.9868	97.77	0.6823	0.000121

Table 3.7. Model rate constants and numerical fit results for (poultry+cow+saw dust) manure, (F_C)

Quantity of (poultry+cow+sawdust) (g)	R^2	RMSE	K	SSE
10- M_1	-2.4633	19.05	0.0001545	3.83
M_2	0.8434	51.21	0.0132	1.16
M_3	0.9831	74.13	0.2331	2.99
M_4	0.9894	58.81	0.2454	1.72
20- M_1	-2.3744	13.33	0.0001945	4.05
M_2	0.8551	46.07	0.0133	1.55
M_3	0.9954	41.83	0.0421	2.09
M_4	0.98885	66.34	0.3144	1.20
30- M_1	-2.4623	18.43	0.0001696	3.51
M_2	0.9165	56.81	0.03512	0.81
M_3	0.9963	41.13	0.1 6232	3.10
M_4	0.9885	61.34	0.33553	1.90
40- M_1	-3.3251	13.04	0.0002615	2.91
M_2	0.9556	37.51	0.0532	1.33
M_3	0.9832	39.81	0.1835	1.94
M_4	0.9734	37.62	0.3473	1.70
50- M_1	-2.3733	11.93	0.0003189	2.03
M_2	0.9185	30.05	0.1663	0.56
M_3	0.9765	24.9	0.2914	1.28
M_4	0.9997	52.69	0.4655	1.29

3.2 Discussion of Result

The soil parameters that were used to characterize the effect of the various amendments used in this study are shown in table 3.1. The initial values of these parameters represent the baseline or starting point for any bioremediation process. Some of the soil parameters were altered after treatment, such parameters include; the soil pH (4.70-8.36), organic carbon (4.33-5.83), organic matter (4.33-5.83) were observed before and after the remediation actions. Increase in some soil parameters before bioremediation could be to the fact that the contaminated soil contains varying proportions of organic carbon while increase in some parameters after bioremediation could be connected to the fact that the nutrient supplements contain some proportions of organic matter, nitrogenous substances e.t.c. Furthermore, at the end of 10 weeks, 79.89%, 81.48% and 84.14% degradation was achieved using NPK fertilizer, poultry manure and poultry+cow+saw dust manure respectively. The result obtained from this investigation shows that the combination of poultry+cow+saw dust manure offers the highest percentage degradation. The removal rates with the later perhaps were feasible due to the presence of sawdust as bulking agent (porous media) that could allow desorption processes as well as biodegradation.

The experimental data was fitted according to the model developed by Oyoh and Osoka (2007) using a curve fitting tool. Also from the numerical fit result of table 3.2- 3.4, it can be deduced that; the specific growth rate (μ) increases with increase in amount of nutrient applied. The specific growth rate (μ) increase was higher at the optimum load of poultry+cow+saw dust manure. YX_0, defines the initial microbial concentration to the final, thus the lower its value the higher the degradation rate. This was observed to decrease steadily as the quantity of manure applied increases. Xo/Y_G is the ratio of the initial microbial concentration to the yield coeeficient. This value was observed to increase with decrease in yield coefficient. It was also observed to increase with increase in amount of manure applied. Increase in Xo/Y_G was more pronounced at the application of (poultry+cow+saw dust) manure though at higher quantity.

The graphs of the kinetic pattern for total hydrocarbon content reduction for the various bio-stimulants employed in this study are shown in Figures 3.16-3.30. In rate modeling and analysis, it is very important to have a realistic measure of reaction rate constant .The higher the rate constants (k) and the correlation coefficients (R^2), the higher the rate of the biodegradation process.

The values of model rate constants k, coefficients of determination R^2, and other parameters as estimated from the model fits are represented in table 3.5-3.7.

The table reveals a positive correlation coefficient R^2 for the reduction in total hydrocarbon content, with high rate constants. From the result obtained, the biodegradation rate constant (k) was higher for the combination of (poultry+cow+saw dust) manure.

It was observed from fig. 3.16-3.30 that 10g, 20g and 30g of both NPK fertilizer and poultry manure fitted well to first order rate model in which the ultimate contaminant concentration is not zero i.e ($S_\infty \neq 0$) but quickly changes trend on the addition of 40g and 50g. Thus as the quantity of fertilizer and poultry manure addition increases the second order rate model is obeyed i.e a case in which ultimate contaminant concentration is zero, ($S_\infty = 0$). A different trend was observed in treatment with a blend of (poultry+cow+saw dust) manure in which the rate model equation 4 (second order rate model with $S_\infty = 0$) is obeyed. It simply mreans that the application of NPK fertilizer and poultry manure at an increased quantity offer similar effect with (poultry+cow+saw dust) manure. This implies that rather than combining biostimulants, poultry manure or NPK fertilizer applied singly at a higher quantity can be used to obtain the same effect when poultry+cow+saw dust is supplied.

IV. CONCLUSSION

This study demonstrates that at optimum load of fertilizer and poultry manure (singly), the rate of microbial growth increases as the level substrate consumed increases. This accord with the result obtained when a combination of (poultry+cow+saw dust) is employed. It was observed that the treatment measures employed in this work followed a first order kinetic rate model with the ultimate contaminant concentration not being zero i.e ($S_\infty \neq 0$) when biostimulants is applied in smaller quantities. But increase in amount of treatment tends to change the reaction towards the second order kinetic rate model with the ultimate concentration assumed zero i.e ($S_\infty = 0$). Therefore, both growth curve model and the kinetic model approach employed in this work provided a good description of an effective bioremediation process.

These observations indicate that the mixture of saw dust, cow dung,and poultry dung (animal source waste) used alone and/or in combination enhanced biodegradation in soil. Similar observations have been reported for the use of plant and animal-derived organic waste (Liu et al., 2012) in the bioremediation of soil contaminated with petroleum hydrocarbons.

The technology for bioremediation that was employed in this study is a simple, effective, inexpensive and environmentally friendly approach, whose biostimulant is readily available, cheap, and is compatible to the environment.

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